The Gibbs paradox and the distinguishability of identical particles

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Abstract

Identical classical particles are distinguishable. This distinguishability affects the number of ways W a macrostate can be realized on the micro-level, and from the relation $S = k \ln W$ leads to a non-extensive expression for the entropy. This result is usually considered incorrect because of its inconsistency with thermodynamics. It is sometimes concluded from this inconsistency that identical particles are fundamentally indistinguishable after all; and even that quantum mechanics is indispensable for making sense of this. In contrast, we argue that the classical statistics of distinguishable particles and the resulting non-extensive entropy function are perfectly acceptable from both a theoretical and an experimental perspective. The inconsistency with thermodynamics can be removed by taking into account that the entropy concept in statistical mechanics is not completely identical to the thermodynamical one. We observe that even identical quantum particles are in some cases distinguishable, and conclude that quantum mechanics is irrelevant to the Gibbs paradox.

I. INTRODUCTION: THE GIBBS PARADOX

Imagine two gas-filled chambers of the same volume, separated by a partition. Both chambers contain equal amounts of the same gas in equilibrium, consisting of the same number N of identical classical particles with the same intrinsic properties. By "identical" we mean that the particles have equal intrinsic properties such as charge and mass. Both parts have the same total energy, temperature T, and pressure. The partition is suddenly removed. What happens to the entropy?

According to thermodynamics the entropy remains the same, because the macroscopic properties of the gases in both chambers do not change. From a thermodynamic point of view, which means restricting ourselves to the consideration of macroscopic properties, nothing happens. If A is the macrostate with the partition in place and B the macrostate without it, the entropy difference is defined as

$$S_B - S_A = \int_A^B \frac{dQ}{T},\tag{1}$$

where dQ is the heat transfer during a quasistatic process from A to B. Because the gases remain in equilibrium, the removal of the partition is a quasistatic process. We have dQ = 0, and hence $S_A = S_B$.

In statistical mechanics the entropy is usually taken to be proportional to the logarithm of the number W of microstates that are compatible with a given macrostate: $S = k \ln W$, where k is Boltzmann's constant. When the partition is removed, the number of available states X per particle doubles: each particle now has twice as much phase space available to it than it had before. Hence, the multiplicity increases from $W_A = X^{2N}$ to $W_B = (2X)^{2N}$, which corresponds to an entropy difference $S_B - S_A = 2kN \ln 2$. This is the Gibbs paradox: The entropy increases according to statistical mechanics but remains the same in thermodynamics.

A traditional way of resolving this paradox is by denying that permutation of identical particles leads to a different state. The real multiplicity is accordingly a factor of N! smaller for a system of N identical particles than what we supposed previously. By the removal of the partition the multiplicity now goes from $W_A = X^{2N}/(N!)^2$ to $W_B = (2X)^{2N}/(2N)!$. With the help of Stirling's approximation it follows that, in the thermodynamic limit $N \to \infty$, $W_B = W_A$, which removes the discrepancy between statistical mechanics and thermodynamics.

However, classical particles are always distinguishable by their positions and trajectories, and thus in classical statistical mechanics there appears to be no reason for the division by N!. According to several authors, quantum theory is therefore needed for justifying this solution of the Gibbs paradox (see, for example, Refs. 2–7). Identical quantum particles seem indistinguishable from the start, because quantum states of systems of identical particles must either be symmetrical under permutation (bosons) or anti-symmetrical (fermions), so that the exchange of particles leaves the state invariant apart from a global phase factor and the multiplicity N! never enters.

If this reasoning were correct, then the Gibbs paradox would imply that the world is quantum mechanical. It is difficult to believe that a thought experiment from classical physics could produce such a profound insight. Unsurprisingly therefore, doubts have been expressed concerning the traditional solution of the paradox. For example, some authors have argued that identical classical particles are also indistinguishable, which would justify the factor 1/N! without recourse to quantum mechanics.^{8–11}

In this paper we follow an argument that is closer to the spirit of classical mechanics. We accept that identical classical particles are distinguishable and that permutation of two of them leads to a different microstate. Nonetheless, we shall show that the Gibbs paradox can be resolved within classical physics. The key to the resolution is the recognition that the entropy concept in thermodynamics is not identical to that in statistical mechanics. This observation will turn out to be sufficient for the resolution of the paradox: neither the indistinguishability of identical particles nor an appeal to quantum theory is needed. On the contrary, even identical quantum particles can sometimes be distinguishable in the sense that is relevant here, so that indistinguishability cannot be relevant to the Gibbs paradox even in quantum mechanics.

II. PERMUTATIONS OF IDENTICAL CLASSICAL PARTICLES

Classical particles, paradigmatically represented by impenetrable spheres, are the example par excellence of distinguishable particles. At each instant of time they can be individually labeled by their different positions. Classical particles follow continuous and non-intersecting trajectories in space-time. Therefore classical particles can be identified over time by their different histories.

Permutation of two identical classical particles produces a different microstate. Imagine a situation in which there is one particle at position x_1 and one at position x_2 . At a later instant there is again one particle at x_1 and one at x_2 . Assume that their respective momenta are the same as before. What has happened in the meantime? There are two possibilities: either the particle that was first at x_1 is again at x_1 and the particle that was first at x_2 is later again at x_2 , or the particles have exchanged their positions. The latter case would be different from the former one, because it corresponds to a different physical process. Although it is true that the two final two-particle states cannot be distinguished on the basis of their instantaneous properties alone, their different histories show that the particle at x_1 in one final situation is not equal to the particle at x_1 in the other final situation.

Given these observations, how can it be that some authors deny that identical classical particles can be distinguished and maintain that permutation does not give rise to a different microstate? One reason is that there is an ambiguity in the meaning of the terms "distinguishable" and "permutation." Consider the following statements: "Two particles are distinguishable if they can always be selectively separated by a filter;" "Two particles are distinguishable if they are first identified as 1 and 2, put into a small box, shaken up, and when removed one can identify which particle was the original number 1." These definitions of distinguishability indeed imply that identical classical particles are always indistinguishable. The concept of "permutation" can similarly be understood in a way that is different from what we have described. Consider again the microstate of two identical particles, one at x_1 and another at x_2 . If the particle at x_2 were at x_1 instead, and the particle at x_1 were at x_2 , with all properties interchanged, there would be no physical differences, neither from an observational point of view nor from the viewpoint of theory. It is therefore reasonable to say that the two situations are the same (see, for example, Ref. 9).

This is a different kind of permutation than the physical exchange we considered previously. In our first example the particles moved from x_1 to x_2 and *vice versa*. Trajectories in space-time connected the initial state to the permuted state. In contrast, in the alternative meaning of permutation, the exchange is not a physical process. Instead, it is an instantaneous swapping that occurs in our imagination, and thus it exchanges nothing but indices and does not need trajectories.

A third sense of permutation is used by Saunders.¹¹ One particle follows trajectory 1 and the other follows trajectory 2. Imagine that the particle that actually follows trajectory 1

instead followed trajectory 2 and *vice versa*. That would result in exactly the same physical situation. As before, this notion of permutation involves the consideration of states before and after the permutation that are not connected by a physical process. A permutation in this sense occurs in our imagination and exchanges an abstract identity (represented by particle indices 1 and 2, respectively) which is independent of the physical characteristics of the situation. This kind of permutation has no physical consequences and cannot be significant for statistical mechanics.

At this point we conclude that if permutation is understood as a physical interchange via trajectories in space-time, then permutations represent physically different possibilities, in the sense of different physical processes that may be realized. However, if permutation is understood differently, then the permutations may not be associated with any physical differences.

III. PERMUTATIONS IN STATISTICAL MECHANICS

Let us now take a closer look at the question of what kind of permutations are relevant to statistical mechanics – physical exchanges with connecting trajectories, or simply swapping indices? Which kind of permutations determine the number of microstates W?

Consider again two gas-filled chambers, each containing N identical particles. Before the partition is removed the number of available states per particle is X. After the partition has been removed, the number of available states is 2X. The reason is that after the partition's removal it has become possible for the particles to move to the other chamber. The doubling of the number of available microstates thus expresses a physical freedom that was not present before the partition was taken away. Trajectories in space-time have become possible from the particles' initial states to states in the other chamber. Particles from the left and right sides can physically exchange their states.

In contrast, even with the partition in place we could imagine the permutation of particles from the left and right sides, but such permutations are not taken into account in the calculation of the multiplicity. Nor do we consider permutations with similar particles outside of the container. In other words, the relevant kind of permutation is the physical exchange, not the swapping of indices.

To completely justify the answer that accessibility via a real physical process, associated

with a connecting trajectory, is the determining factor in the calculation of multiplicities, we would have to consider the foundations of statistical mechanics. An important approach in this area is ergodic theory, in which the probability of a macrostate is argued to be proportional to its multiplicity on the grounds that the multiplicity is a measure of the time a system actually spends in that part of phase space corresponding to the macrostate in question. This argument makes sense only if the microstates in this part of the phase space are actually accessible by physical processes. Microstates that give rise to the same macrostate but cannot be reached from the initial microstate through the evolution of the system are irrelevant for the macrostate's probability.

Although the original form of the ergodic hypothesis (according to which all microstates are actually visited in a relatively short time) has proven to be untenable, the basic idea that accessibility is the criterion for the relevance of microstates is still essential. The multiplicities that occur in more recent and sophisticated approaches to the foundations of statistical mechanics are the same as those of the original ergodic theory.

We therefore conclude that the multiplicity of a macrostate in classical statistical mechanics is given by the number of ways that the macrostate can be reached by a physical process. Permutations, corresponding to physical exchanges, represent different and real physical possibilities. We must therefore not divide by N! when calculating multiplicities of macrostates of identical classical particles.

IV. EMPIRICAL CONSEQUENCES OF NOT DIVIDING BY N!

The foregoing argument for not dividing by N!, plus the relation $S = k \ln W$, makes the statistical mechanical entropy non-extensive. For example, after the removal of the partition the total entropy is not twice the entropy each single chamber had before, but is larger by the amount $2kN \ln 2$.

There are three kinds of objections against not dividing by N! and the non-extensivity of the statistical entropy that is its consequence: (1) it leads to incorrect empirical predictions;^{2,12,13} (2) it leads to a violation of the second law of thermodynamics;^{4,6,14} and (3) it leads to a discrepancy with the thermodynamic entropy.

In this section we address the first of these objections. The second and the third, the Gibbs paradox proper, are discussed in Secs. V and VI.

In contrast to what is claimed by some authors, 2,12,13 dividing or not dividing the number of microstates by N! is irrelevant to the empirical predictions of statistical mechanics for isolated systems. That is, although there is no fundamental justification for dividing by N! on the basis of particle indistinguishability, a systematic division by N! for all particles of the same kind in mutually accessible states has no empirical consequences. This conclusion follows because all empirical predictions made by statistical mechanics rest ultimately on the probabilities assigned to macrostates. These probabilities are calculated with the help of the fundamental assumption that in equilibrium the accessible microstates in an isolated system are all equally probable, so that the probability of a macrostate is its multiplicity divided by the total number of microstates. In isolated systems no particles can move in or out, so that the number N of particles remains constant which means that not only are all multiplicities decreased by the factor of 1/N!: the same happens to the total number of microstates if we decide to systematically divide by N!. The probability of a macrostate is therefore not affected, and whether we divide the multiplicity by N! or not makes no difference for empirical predictions.

Statistical mechanics does not only describe systems with a constant number of particles. Systems in which particles can move in and out can also be treated, as is done with the grand canonical ensemble, where the probability distribution can be derived by considering a system with varying particle numbers as part of a larger particle reservoir. This reservoir is again isolated, and the fundamental assumption is now applied to this larger system. Therefore our conclusion that the empirical predictions remain the same, whether we systematically divide by N! or not, also applies to systems in which particles are exchanged between subsystems (in agreement with what was argued in Ref. 15).

Particle numbers can also change by chemical reactions, where the number of molecules of a certain kind need not be constant, even if the system is isolated. For such a system division by the number of permutations of the elementary constituents (in this case the atoms) does not matter for the empirical results because the numbers of atoms from which the molecules are composed remain constant, as discussed in Ref. 16.

To illustrate that the factor 1/N! does not matter for empirical predictions, we consider the example given in Ref. 13.¹⁷ Two containers, one of volume V_1 and the other of volume V_2 , are separated by a wall. Both contain the same kind of ideal gas, consisting of identical classical particles. Now a hole is poked in the wall and the particles can move to the other container. After some time equilibrium is reached. What is the number of particles in the volume V_1 in equilibrium? From standard classical statistical mechanics, with the factor 1/N! included in the multiplicity, the empirical prediction follows that $N_1 = NV_1/(V_1 + V_2)$, where N_1 is the number of particles in V_1 and N is the total number of particles. According to Ref. 13, if the factor 1/N! were not included, an incorrect empirical prediction would be obtained if V_1 is not equal to V_2 : all particles would go to the larger of the two volumes.

However, as we shall now demonstrate, consistently taking into account the particles' distinguishability does lead to the correct predictions using $S = k \ln W$. In Ref. 13 empirical predictions were obtained by calculating in what macrostate the entropy is maximal, and we take the same approach here.

Consider a macrostate of the ideal gas, defined by the observable N_1 . As a constraint we take that the total number of particles is N, so that $N - N_1$ particles are in volume V_2 . The multiplicity is given by

$$W = c V_1^{N_1} V_2^{N-N_1} \frac{N!}{N_1!(N-N_1)!},$$
(2)

where c is a factor independent of the volume and the number of particles. The factor $N!/(N_1!(N-N_1)!)$ is included because it is the number of ways N_1 distinguishable particles can be chosen out of N particles. With $S = k \ln W$ and Stirling's approximation $\ln N! \approx N \ln N - N$, we find for the entropy

$$S = kN_1 \ln V_1 + k(N - N_1) \ln V_2 + kN \ln N - kN_1 \ln N_1 - k(N - N_1) \ln(N - N_1) + k \ln c.$$
(3)

In equilibrium S is a maximum, so N_1 in equilibrium can be found by solving $\partial S/\partial N_1 = 0$. The solution is $N_1 = NV_1/(V_1 + V_2)$, which is the same empirical prediction as obtained with the factor 1/N! included.

Note how the non-extensivity of the entropy $S = k \ln W$ proves essential for a consistent use of this expression for the entropy. When a hole is made in the wall, particles in volume V_1 may exchange their positions with particles in the other volume, so the multiplicity increases as indicated in Eq. (2). That means that the entropy becomes larger than the sum of the two original entropies of V_1 and V_2 , just as in the case of the Gibbs paradox.¹⁸

V. SECOND LAW OF THERMODYNAMICS

The second alleged problem is that the non-extensivity of the entropy leads to a violation of the second law of thermodynamics.^{4,6,14} Consider again the two chambers after the partition has been removed. When the partition is returned, the entropy decreases by $2kN \ln 2$. But the second law insists that entropy cannot decrease!

An important issue here is the nature of the second law in its statistical version: it will turn out that to solve the just-mentioned problem we need to recognize that the second law in thermodynamics is not exactly the same as the second law in statistical mechanics.

In thermodynamics the second law says that the entropy does not decrease if there is no heat transfer to or from the environment. For the case of the replacement of the partition there is no such heat transfer, so the thermodynamic entropy should not decrease.

In contrast, in statistical mechanics the second law expresses a probability consideration: equilibrium macrostates possess a probability vastly greater than that of non-equilibrium states, and therefore it is enormously probable that the system will reach equilibrium and subsequently stay in equilibrium. The number of microstates corresponding to the equilibrium macrostate is virtually equal to the total number of accessible microstates W, which is the justification for the use of $S = k \ln W$ as the entropy belonging to the equilibrium state. That the statistical mechanical entropy S, with $S = k \ln W$, does not decrease is a direct expression of the dominance of the most probable macrostate. Accordingly, the second law of statistical mechanics states that the entropy of a system goes, with overwhelming probability, to the maximum value compatible with the total number of accessible microstates, and will not decrease as long as this number of accessible states does not decrease. The statistical second law tells us, for instance, that without intervention from outside not all particles will move to the same corner of the container. But it does not tell us how W may change when the system is manipulated from outside, for example by placing a partition in it.

VI. SOLUTION OF THE GIBBS PARADOX

The paradox is that upon removal of the partition between the two containers the entropy increases according to classical statistical mechanics, whereas it remains the same in

thermodynamics. What we have seen is that for classical particles the entropy should really increase in statistical mechanics, in the sense that the number of accessible microstates W does increase. This increase reflects the redefinition of the system, and of W that results from manipulation from outside (the removal of the partition). The statistical second law only plays a role here to the extent that it says that the system will assume an equilibrium state which is compatible with this new and increased W. In principle, we could empirically verify that the number of microstates has actually increased by following the paths of individual particles (we could in this way give empirical content to the existence of the entropy of mixing.¹⁹) But this verification would require measurements on the microscopic level that would lead us outside the domains of thermodynamics and statistical mechanical predictions (in which the precise microstate is assumed to be immaterial). As we have seen in Sec. IV, as long as we remain within the realm of the usual macroscopic measurements, the increase of the entropy, for gases of the same kind, will not lead to any new empirical consequences.

Is there a problem here? Can we not just accept that the entropy changes in statistical mechanics and remains the same in thermodynamics? Yes, we can. We only have to take into account that the entropy is defined differently in statistical mechanics than in thermodynamics. In statistical mechanics the existence of a micro-description is taken into account as a matter of principle, whereas in thermodynamics this same micro-description is excluded from the start. As we have seen, the consequence is an increase of entropy according to statistical mechanics, but its direct empirical significance is only on the micro-level and does not lead to any new predictions for macroscopic measurements. The difference between the statistical mechanical and the thermodynamic definition of entropy makes it understandable that the values of entropy changes in statistical mechanics are sometimes different from those in thermodynamics.

There are no conflicts with the second law here. According to both statistical mechanics and thermodynamics, the second law is obeyed perfectly. The statistical mechanical account is that the number of microstates increases through intervention from outside (the removal of the partition), and the statistical second law tells us that the system will subsequently make maximum use of the increased area in phase space. Therefore, the prediction is that the system will exhibit equilibrium values of its macroscopic quantities, so that on the macro-level nothing changes. In thermodynamics this "fine-grained" consideration plays

no role: nothing changes and according to the thermodynamic second law the entropy remains constant. Both descriptions are valid within their own context and lead to the same predictions.

The same type of argument can be used if we consider what happens when the partition is replaced. According to thermodynamics nothing happens to the entropy, because there is no exchange of heat. According to statistical physics, there is a decrease of W and thus of the entropy. But this decrease does not mean a violation of the second law! The decrease in W is a consequence of the redefinition of the accessible phase space caused by intervention in the system. The statistical second law remains valid, and predicts that the two subsystems will fully make use of their phase space possibilities (which in this case means that equilibrium will be maintained).

From a pragmatic point of view it is useful if thermodynamics and statistical mechanics give exactly the same entropy values. We can achieve this equivalence by introducing a new entropy definition in statistical mechanics: Replace $S = k \ln W$ by $S = k \ln(W/N!)$. For systems in which N is constant this new definition makes no difference for any empirical predictions, because it only adds a constant number to the entropy value. For the Gibbs case, in which N does change, this adaptation of the definition leads to the disappearance of the mixing term and therefore to extensivity of the entropy in the limit $N \to \infty$. In this way agreement with thermodynamics is obtained.

It is important to realize that the introduction of this "reduced entropy" (as it is called by Cheng²⁰), is motivated by the wish to preserve this agreement: its justification is in the reproduction of thermodynamic entropy values under all conditions, even though the basic assumptions of statistical physics are different from those of thermodynamics. It is certainly reasonable to change the definition of the statistical mechanical entropy to achieve agreement with thermodynamics. There is nothing wrong with the reduced entropy if it is interpreted from this pragmatic point of view. But it would be a mistake to interpret the division by particle number factorials as a necessary consequence of a fundamental feature of microscopic physical reality, namely the indistinguishability of particles of the same kind.

VII. DISTINGUISHABLE IDENTICAL QUANTUM PARTICLES

In contrast to classical particles, identical quantum particles are usually assumed to be indistinguishable as a matter of principle. This fundamental indistinguishability is supposed to be the result of the quantum mechanical (anti-)symmetrization postulates, where permutations of the indices in the quantum mechanical many-particle formalism leave a state either invariant (for bosons) or change its sign (for fermions).

As we have argued, the permutations that are relevant to statistical mechanics are not simply permutations of indices, but rather processes by which the permuted state is connected to the initial state by trajectories in space-time. Quantum mechanics allows situations in which definite particle trajectories through space-time can be defined. When the individual one-particle wave packets in the many-particle state have small spatial extensions and do not overlap, we can identify them over time (and by Ehrenfest's theorem they approximately follow the paths of classical particles). In the classical limit of quantum mechanics such narrow wave packets come to represent the particles we know from classical physics. Permutation of trajectories of such wave packets in the physical sense discussed before produces a different state, just as in classical physics. However, we have all been taught that quantum particles of the same kind are fundamentally indistinguishable – so how can it be true that it may make sense to speak about a physical interchange of them?

The confusion results from an ambiguity in how the particle concept is used in quantum mechanics. Sometimes the indices in the many-particle formalism are taken to refer to particles so that everything is symmetrical and all particles are in exactly the same state (as follows from taking partial traces to define the one-particle states). But there is also another use of the particle concept in which individual wave packets are taken to represent single particles. It is this second way of thinking about particles, and not the first one, that in the classical limit gives the particles we know from classical physics. ^{19,21,22} Classical particles emerge from quantum mechanics when wave packets become localized in the classical limit. It is only then that the classical particle concept becomes applicable (see Ref. 22 for an extensive discussion).

Narrow wave packets can follow trajectories through space-time, and as long as they remain separated from each other, these wave packets remain as distinguishable as classical particles. When a quantum particle represented by such a wave packet moves from x_1 to x_2

and another particle of the same kind moves from x_2 to x_1 , then the final state is different from the initial state just as in our earlier discussion on classical particles.

As we have argued, the Gibbs paradox can be resolved without invoking the indistinguishability of particles. We see that quantum theory does not change the relevant characteristics of the situation, so that quantum theory is irrelevant to the resolution of the paradox. It does not matter if we switch to the quantum description of the gases we have considered in the context of the paradox. If the particles are (approximately) localized, permutation produces a different microstate just as in classical mechanics.

It is interesting to compare our arguments with those of Saunders, ¹¹ who regards even classical particles as indistinguishable. According to Saunders there is one reason why classical particles are generally assumed to be distinguishable: "... we surely can single out classical particles uniquely, by reference to their trajectories. But there is a key objection to this line of thinking: so can quantum particles, at least in certain circumstances, be distinguished by their states." We agree with this conclusion, but we do not see it as an objection. Saunders' conclusion is that "indistinguishability (permutability, invariance under permutations) makes just as much sense classically as it does in quantum mechanics." We say the opposite: distinguishability often makes just as much sense for quantum particles as for classical particles.

VIII. CONCLUSION

The Gibbs paradox should not be interpreted as providing an argument for the indistinguishability of identical classical particles. Classical particles can be distinguished by their different positions and their different trajectories through space-time. Nor does the Gibbs paradox needs quantum mechanics for its solution: identical quantum particles can be as distinguishable, in the relevant sense, as classical particles.

One way of resolving the Gibbs paradox is by recognizing that entropy and the second law have slightly different meanings in statistical mechanics and in thermodynamics. In thermodynamics the entropy has to be extensive; but this is not necessarily so in statistical mechanics. It is possible, and even advisable, to make the statistical mechanical entropy extensive by introducing a new entropy definition (the reduced entropy) that does not change predictions as long as these predictions remain within the realm of thermodynamics. But

this convention has nothing to do with any fundamental indistinguishability of identical particles.

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- ⁵ A. Sommerfeld, *Thermodynamik und Statistik* (Deutsch, Thun, 1977), pp. 194–195, 216–218.
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- Reference 13 also denies that classical particles should be treated as indistinguishable. In contrast, Ref. 13 claims that use of the Boltzmann entropy $S = k \ln W$ leads to incorrect predictions for distinguishable particles.
- ¹⁸ If this non-extensivity is not taken into account, incorrect predictions are obtained when $S = k \ln W$ is used. See Ref. 13.
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